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FILE: H₂ GENERATOR

July 27, 1957

PROGRESS REPORT ON LITHIUM HYDRIDE
GENERATOR

In a previous report operation of this generator on a 2 liter scale and a design of a full-scale model were described. It was then decided to advance to a 20 liter scale in glass and to find answers to certain other questions, namely: what was the hazard to the operator from metallic hydrides such as arsine, what was the likelihood of explosion in case of an accident to the generator, and what was the temperature dependence of the reaction rate.

20-liter generator:

This was a faithful scale-up of the 2-liter generator previously used and described. It was operated only once, and in this operation self-sustaining reaction was never obtained. This failure was due to mechanical difficulties. The metal frame in which the generator was mounted was insufficiently rigid, and the vibration resulting from the initial reaction broke off the elbow of the tube leading to the pump. Before this happened, however, the pump was working and bringing up large volumes of water. After the break occurred operation was continued by pouring in water by hand. The reaction was thus completed in 20 minutes.

Aside from the accident, nothing was observed which would indicate any likelihood of serious difficulty with a second model on this scale. Everything else appeared to go exactly

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as in the 2-liter model.

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Danger of Fire and Explosion:

A two-liter flask full of lithium hydride floating bottom-up in a pond was hit with a 30-caliber rifle bullet at a terminal velocity of about 3,000 feet per second. The flask was shattered and there was a puff of smoke as the lithium hydride hit the water, but there was no fire. The lithium hydride fragments spread out over the surface of the water and there was considerable noise and a visible pillar of smoke upward, but no flame was observed.

At this point I was convinced that lithium hydride could not be made to inflame by contact with water, and worked beside the twenty liter generator with complete confidence. However, during this experiment several chunks of lithium hydride came out through the pump, as is usual, and hissed about in the open air. One of these caught fire. This is the first time I have seen this happen, and I have no explanation for it. The matter requires further investigation before the apparatus can be considered completely safe.

Toxicity:

Hydrogen from these samples of lithium hydride is by no means odorless, smelling somewhat like the gas from calcium carbide, and this lead to the question whether it might not be toxic due to compounds like arsine. At the time of the test with the 20 liter apparatus I breathed fair amounts of this gas without ill effects. I would not have taken this chance except for the following test which had been previously made.

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The hydrogen from two liters of lithium hydride was passed through a weighed vycor tube kept during the experiment at red heat in a muffle furnace. The passage of the gas required three days. No smudge appeared on the tube and its weight remained the same to within .1 mg.

A priori this would indicate that the lithium hydride contained less than 1 part per million of arsenic and antimony, but this is subject to the assumption that arsine and stibine are completely decomposed by heat - that the reaction was not reversible. A thermodynamic calculation based on the heat of formation of arsine and an estimate of the entropies involved indicated that the equilibrium pressure of arsine in the presence of 1 atmosphere pressure of hydrogen and solid arsenic at 500 C. should be of the order of 10^{-15} . It is therefore concluded that there was less than one part per million of arsenic in this hydrogen, based on the weight of lithium hydride used. Since stibine is known to be less stable than arsine the same remark applies to antimony. This conclusion cannot be drawn for phosphorous, however, as the equilibrium pressure of phosphine in equilibrium with phosphorous and hydrogen is considerably greater than for arsine.

Reaction Rate:

The temperature coefficient of the rate of reaction of lithium hydride with water is important in that it determines the stability of the generation. A large positive temperature coefficient of the reaction rate would imply the possibility

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of a runaway reaction. Actually, this temperature coefficient was found to be slightly negative, in accord with the observed stability.

The reaction rate was measured by observing the time required to dissolve a piece of lithium hydride of known weight in water of known constant temperature. Assuming that at a given temperature the rate of reaction is proportional to the surface area of the amount of lithium hydride remaining at that time, and that the piece dissolves at constant shape, it is found that the time for complete solution should be proportional to the cube root of the initial weight. The scatter between the results of individual experiments was too great to establish quantitative agreement or disagreement with this theory, but it is in at least qualitative agreement with the observed facts. It is believed that the scatter is due, in part at least, to the fact that the pieces of lithium hydride in different experiments were not of exactly the same shape.

It has been realized from the start of this work that the rate of solution is dependent on the concentration of lithium hydroxide in the water used. It takes days for a 2 gram piece of lithium hydride to dissolve in saturated lithium hydroxide solution at room temperature, whereas the same piece dissolves in about 4 minutes in a large volume of pure water. This relationship has not been fully explored, but it has been found that at 0 C. the reaction rate in half-saturated lithium hydroxide solution is .8 times that in dilute lithium hydroxide solution, and that at 100 C the rate in half-saturated solution is .4

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times what it is in the dilute solution. The experimental error, as determined by least squares treatment of the results, is such that the difference at 0 C is barely established, but the difference at 100 C is definite. From these results it is concluded that the effect of changing concentration of lithium hydroxide as pieces of lithium hydroxide no larger than 6 grams are dissolved in a liter of initially pure water on the rate of solution is negligible compared with the scatter between individual determinations, which is of the order of a factor of 1.3. When a piece of lithium hydroxide weighing 6 grams is dissolved in a liter of water the final concentration of lithium hydroxide is 14 grams per liter, as compared with a saturation value of 68 grams per liter at 0 C and 94 grams per liter at 100 C.

Initial experiments were made in a thermostat until it was found that the temperature coefficient was small compared with the spread between individual and supposedly duplicate experiments; thereafter they were made in a two liter beaker on the bench (for experiments at 20 C.), packed in ice for experiments at zero C, and boiling on a hot plate in experiments at 100 C. In experiments at nominal 20 C. the actual temperature was taken as the mean of the initial and final temperatures. More than 100 individual experiments were made and the results reduced by the method of least squares. The final results may be summarized as follows, relative to the rate at 0 C in initially pure water.

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Summary of Reaction Rate Data

Centigrade Temperature	Initially pure water	50% saturated lithium hydroxide
0	$1.0 \pm .2$	$.8 \pm .2$
20	$1.2 \pm .1$	- - - -
100	$.8 \pm .1$	$.4 \pm .2$

These are relative rates. Absolute rates may be computed from these (in seconds) by multiplying by 200 times the cube root of the weight of the piece in grams. This gives the total time to dissolve. Thus, a piece weighing 6 grams would be expected to dissolve in pure water initially at 20 C in approximately 290 seconds, and under the same conditions a piece weighing initially .2 grams in approximately 95 seconds.

Few individual pieces of the lithium hydride used weighed more than 6 grams. Assuming the generator to operate at 100 C and with a water supply such that the effluent was half saturated, the reaction could be completed in approximately 18 minutes. This is in accord with the reaction times in the generator observed during my fastest runs. It would appear that the practical speed of generation is about equally limited by the rate of reaction and the rate at which the hydrogen can be handled.

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Since the rates of chemical reactions often have large positive temperature coefficients it may seem strange that this one shows a small negative coefficient. It is possible, however, to see physically why this is so, or at least to give it a certain physical plausibility. Suppose that the reaction rate of the hydride with water, either liquid or vapor, is so fast that the rate-controlling step is transport of water to the hydride surface. Since lithium hydroxide is only moderately soluble in water the reaction always produces a coating of solid lithium hydroxide on the piece being dissolved. This coating is visible, and when the reaction is interrupted and a piece taken out and broken it is seen that this coating may be as much as 1/20 inch thick. Since the reaction proceeds even when this coating is visually intact it follows that water - liquid or vapor - must be getting in through cracks or small holes in the coating. Hydrogen must be coming out through these same cracks or holes at the same time. Thus the flow of hydrogen out opposes the flow of water in. At low temperatures the volume of the hydrogen coming out is essentially its dry volume. At temperatures near the boiling point of water what comes out is a mixture of hydrogen and steam, and has a volume several times the dry volume of the contained hydrogen. Thus there is more impedance to the flow of water in to the hydride and the rate of the reaction tends to that extent to be lower than at the lower temperature.

The apparent maximum in the reaction rate at intermediate temperatures can be made plausible as follows: At temperatures to 50 C or ^{lower} ~~higher~~ the vapor pressure of water is so low that the the volume of the escaping hydrogen is essentially the dry

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volume. Thus the mechanism cited in the foregoing paragraph, and which would tend to reduce the rate of the overall reaction, has little effect. But in this comparatively low temperature range the viscosity of water is decreasing rapidly with increasing temperature. Thus it is plausible that the rate of the overall reaction should at first increase with temperature and later decrease as the volume of water vapor which evaporates into the hydrogen becomes a factor.

As to the effect of lithium hydroxide concentration on the reaction rate it is plausible that this should be small to approximately half-saturation and decisive above that. The presence of lithium hydroxide in the solution decreases the rate at which lithium hydroxide dissolves from the skin around the piece. The rate of solution would be expected to be approximately proportional to the difference between the actual concentration and the saturation concentration. Percentagewise, this rate should thus be little affected by unit changes in concentration at concentrations below half saturation, but much affected by changes of the same unit near saturation. This is in qualitative accord with the observed facts.

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